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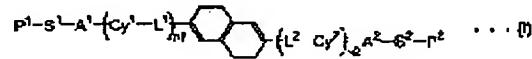
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(54) POLYMERIZABLE LIQUID CRYSTALLINE COMPOUND, LIQUID CRYSTAL POLYMER AND USE THEREOF

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a polymerizable liquid crystalline compound which has excellent refractive index anisotropy and a wide transparent range and hardly receives a cis-trans transfer caused by UV light, to provide a liquid crystal polymer comprising the polymerizable liquid crystalline compound, to provide an optical phase difference film and an optical isomer each having large refractive index anisotropy, and to provide a nonlinear optical element and an electrooptic element each having a wide transparent range and hardly receiving a cis-trans transfer caused by light.

SOLUTION: This polymerizable liquid crystalline compound is represented by the general formula (1)



(P1 and P2 are each independently a polymerizable group; A1, A2, L1 and L2 are each independently a divalent connecting group comprising a single bond, O, S, carbonyl, sulfonyl, a substituted or unsubstituted imino or their mixture; S1 and S2 are each independently a divalent connecting group; Cy1 and Cy2 are each independently a 5 to 14C cyclic group; n1 and n2 are each such an integer that n1+n2 is 0 to 2).

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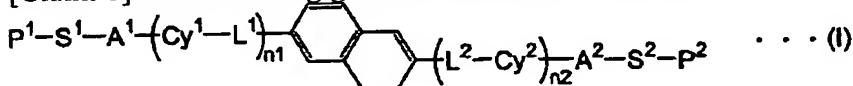
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## CLAIMS

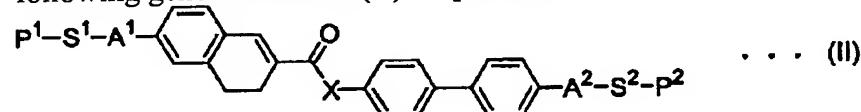
[Claim(s)]

[Claim 1] The following general formula (I): [Formula 1]



(P1 and P2 express a polymerization nature machine independently among a general formula (I), respectively.) Independently A1, A2, L1, and L2, respectively Single bond, an oxygen atom, a sulfur atom, The divalent connection radical which consists of the imino groups or such combination which are not permuted [ a carbonyl group, a sulfonyl group, a permutation, or ] is expressed. S1 and S2 express a divalent connection radical independently, respectively, Cy1 and Cy2 express the annular radical of the carbon atomic numbers 5-14 independently, respectively, and n1 and n2 express the integer from which n1+n2 turn into 0-2. The polymerization nature liquid crystal compound characterized by what is expressed.

[Claim 2] a polymerization nature liquid crystal compound according to claim 1 -- setting -- following general formula (II): -- [Formula 2]



(P1 and P2 express a polymerization nature machine independently among a general formula (II), respectively.) Independently A1 and A2, respectively Single bond, an oxygen atom, a sulfur atom, a carbonyl group, the divalent connection radical which consists of the imino groups or such combination which are not permuted [ a sulfonyl group, a permutation, or ] is expressed, S1 and S2 express a divalent connection radical independently, respectively, and X expresses the imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ]. The polymerization nature liquid crystal compound characterized by what is expressed.

[Claim 3] The polymerization nature liquid crystal compound characterized by at least one of said P1 and said P2 [ the ] being an acryloyloxy radical or a methacryloyloxy radical in a polymerization nature liquid crystal compound according to claim 1 or 2.

[Claim 4] It is the polymerization nature liquid crystal compound which one side is an imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ] among said A1 and said A2, and is characterized by another side being carbonyloxy group or a sulfonyloxy radical in a polymerization nature liquid crystal compound according to claim 1 to 3.

[Claim 5] The liquid crystal polymer characterized by a polymerization nature liquid crystal compound according to claim 1 to 4 coming to carry out a polymerization.

[Claim 6] The liquid crystal constituent characterized by including a polymerization nature liquid crystal compound and a solvent according to claim 1 to 4.

[Claim 7] Optical phase contrast film characterized by containing a liquid crystal polymer according to claim 5.

[Claim 8] The optically anisotropic body characterized by containing a liquid crystal polymer according to claim 5.

[Claim 9] The nonlinear optical element characterized by containing a liquid crystal polymer according to claim 5.

[Claim 10] The electro-optics component characterized by containing a liquid crystal polymer according to claim 5.

[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

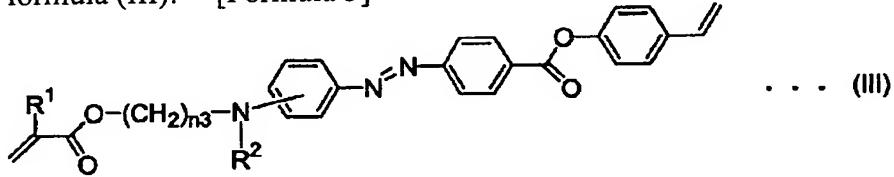
[0001]

[Field of the Invention] This invention relates to the optical phase contrast film using a polymerization nature liquid crystal compound useful as photoelectron high-performance material, a liquid crystal polymer, and this polymer, an optically anisotropic body, a nonlinear optical element, and an electro-optics component.

[0002]

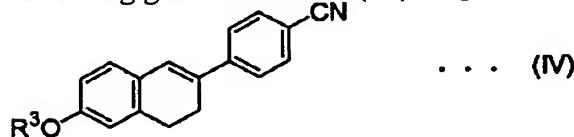
[Description of the Prior Art] Since the liquid crystal compound which has a polymerization nature machine serves as an optically anisotropic body easily by carrying out a polymerization in the state of liquid crystal, it is used for optical elements, such as an optical compensating plate (phase contrast plate) of a liquid crystal display, and an optical head, for example, is used for the optical compensating plates (EP No. 0,423,881 etc.) of a STN liquid crystal display, polarization beam splitters (EP No. 0,428,213 etc.), etc. The suitable liquid crystal compound for these optical elements is indicated by the patent reference 1 - 4 grades. However, the conventional polymerization nature liquid crystal compound may have a low refractive-index anisotropy by the gestalt of use, or wavelength dispersion nature may not suit. Therefore, development of the polymerization nature liquid crystal compound with which a refractive-index anisotropy and wavelength dispersion nature have been improved is desired.

[0003] Moreover, the polymerization nature liquid crystal compound which has a nonlinear optics property can be used as an organic non-linear optical material. JP,11-322690,A -- following general formula (III): -- [Formula 3]



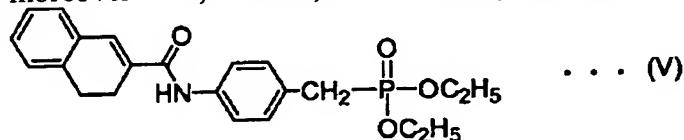
(-- R1 expresses a hydrogen atom or a methyl group among a general formula (III), R2 expresses a low-grade alkyl group, and n3 expresses four or more integers.) -- the compound expressed is indicated. However, since these compounds have azo association in intramolecular, a transparency field is narrow, and since it is further easy to receive the cis--transformer transition by ultraviolet radiation, an improvement is desired.

[0004] in addition -- as the compound which has a hydroxy naphthalene frame -- JP,59-163358,A -- following general formula (IV): -- [Formula 4]



(-- R3 expresses the alkyl group or acyl group which is not permuted [ a permutation or ] among a general formula (IV).) -- the compound expressed is indicated. Although this compound is a liquid crystal compound, since it does not have the polymerization nature machine, it is inferior to stability.

moreover -- JP,8-73486,A -- following type (V): -- [Formula 5]



The phosphoric ester compound which is alike and is expressed more is indicated. However, this compound is not a polymerization nature liquid crystal compound.

[0005]

[Patent reference 1] The Europe patent application public presentation No. 0,261,712 specification

[the patent reference 2] The Europe patent application public presentation No. 0,331,233

specification [the patent reference 3] The Europe patent application public presentation No. 0,405,713 specification [the patent reference 4] International public presentation/[ 93rd ] No. 22397 pamphlet [0006]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention has the outstanding refractive-index anisotropy etc., its transparency field is large, and the polymerization nature liquid crystal compound which cannot receive the cis--transformer transition by ultraviolet radiation easily, and this polymerization nature liquid crystal compound are offering the liquid crystal polymer which comes to carry out a polymerization.

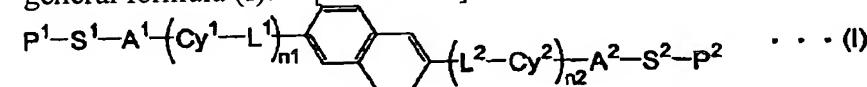
[0007] Another purpose of this invention is offering the optical phase contrast film and an optically anisotropic body with a large refractive-index anisotropy.

[0008] It is offering the nonlinear optical element and electro-optics component which cannot receive cis--transformer transition of this invention another purpose's has a still larger transparency field, and according to light easily.

[0009]

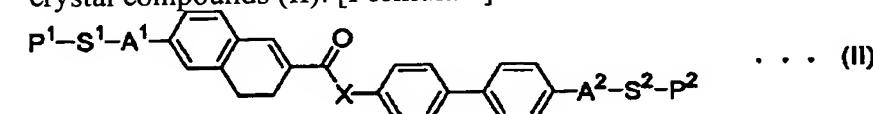
[Means for Solving the Problem] In view of the above-mentioned purpose, the new polymerization nature liquid crystal compound which has the structure of specification [ this invention person ] is excellent as photoelectron high-performance material wholeheartedly as a result of research, and it was stable in the optical phase contrast film and an optically anisotropic body with a large refractive-index anisotropy, and the list, and it discovered giving a nonlinear optical element with a large transparency field, and an electro-optics component, and hit on an idea to this invention.

[0010] namely, the polymerization nature liquid crystal compound of this invention -- following general formula (I): -- [Formula 6]



(P1 and P2 express a polymerization nature machine independently among a general formula (I), respectively.) Independently A1, A2, L1, and L2, respectively Single bond, an oxygen atom, a sulfur atom, The divalent connection radical which consists of the imino groups or such combination which are not permuted [ a carbonyl group, a sulfonyl group, a permutation, or ] is expressed. S1 and S2 express a divalent connection radical independently, respectively, Cy1 and Cy2 express the annular radical of the carbon atomic numbers 5-14 independently, respectively, and n1 and n2 express the integer from which n1+n2 turn into 0-2. It is characterized by what is expressed.

[0011] The following general formula among the above-mentioned polymerization nature liquid-crystal compounds (II): [Formula 7]



(P1 and P2 express a polymerization nature machine independently among a general formula (II), respectively.) Independently A1 and A2, respectively Single bond, an oxygen atom, a sulfur atom, a carbonyl group, the divalent connection radical which consists of the imino groups or such combination which are not permuted [ a sulfonyl group, a permutation, or ] is expressed, S1 and S2

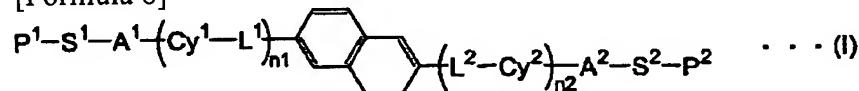
express a divalent connection radical independently, respectively, and X expresses the imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ]. The polymerization nature liquid crystal compound expressed is desirable.

[0012] The polymerization nature liquid crystal compound expressed by a general formula (I) or (II) is (1). (2) when at least one of P1 and the P2 is an acryloyloxy radical or a methacryloyloxy radical. One side is the imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ] among A1 and A2, and when another side is carbonyloxy group or a sulfonyloxy radical, the especially excellent photoelectron function can be demonstrated.

[0013]

[Embodiment of the Invention] [1] the polymerization nature liquid crystal compound of polymerization nature liquid crystal compound this invention -- following general formula (I): --

[Formula 8]



It is alike and is expressed more.

[0014] P1 and P2 express a polymerization nature machine independently among a general formula (I), respectively. As a polymerization nature machine, although the example is indicated by the p.409 grade in a "liquid crystal handbook", Maruzen, and 2000, an acryloyloxy radical, a methacryloyloxy radical, a glycidyl group, a vinyloxy radical, etc. are mentioned, for example. As for at least one of P1 and the P2, it is desirable that they are an acryloyloxy radical or a methacryloyloxy radical, and, as for both P1 and P2, it is more desirable that they are an acryloyloxy radical or a methacryloyloxy radical.

[0015] A1, A2, L1, and L2 express the divalent connection radical which consists of the imino groups or such combination which are not permuted [ single bond, an oxygen atom, a sulfur atom a carbonyl group, a sulfonyl group, a permutation, or ] independently, respectively. As for A1 and A2, it is desirable respectively that it is the imino group which is not permuted [ an oxygen atom, a sulfur atom carbonyloxy group (-COO-), an oxy-carbonyl group (-OCO-), a sulfonyloxy radical a permutation, or ] independently. More preferably, one side is an imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ] among A1 and A2, and another side is carbonyloxy group (-COO-) or a sulfonyloxy radical. Respectively, as for L1 and L2, it is desirable that they are single bond, carbonyloxy group (-COO-), an oxy-carbonyl group (-OCO-), a carbonyl imino group (-CONH-), or an imino carbonyl group (-NHCO-) independently, and it is more desirable that they are single bond, carbonyloxy group (-COO-), or an oxy-carbonyl group (-OCO-). When using the polymerization nature liquid crystal compound of this invention for a nonlinear optical element or an electro-optics component, as for L1 and L2, it is desirable respectively that they are single bond or carbonyloxy group independently.

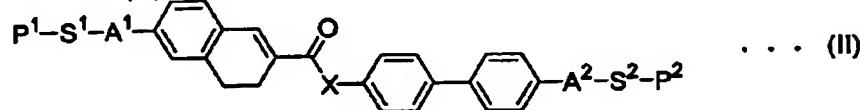
[0016] S1 and S2 express a divalent connection radical independently, respectively. Even if S1 and S2 contain the hetero atom and they include the ring structure, they may have the substituent. As a desirable example of this substituent, a low-grade alkyl group and halogen atom etc. is mentioned. When the carbon atom which has a substituent serves as asymmetrical carbon, which configuration is sufficient among R, S, and RS. As for S1 and S2, it is desirable respectively that it is the divalent connection radical of the carbon atomic numbers 2-14, and it is more desirable that it is the alkylene group of the carbon atomic numbers 2-10.

[0017] Cy1 and Cy2 express the annular radical of the carbon atomic numbers 5-14 independently, respectively. A monocycle or polycyclic (the condensed ring, ring set) are sufficient as Cy1 and Cy2, and a non-aromatic ring or an aromatic series ring is sufficient as them. Cy1 and Cy2 may have a substituent on a ring, and the substituent is the low-grade alkoxy group or halogen atom of the low-grade alkyl group of the carbon atomic numbers 1-6, and the carbon atomic numbers 1-6 preferably, and they are a methyl group, a chlorine atom, or a bromine atom more preferably. As for Cy1 and Cy2, it is desirable respectively that they are the benzene ring or a naphthalene ring, and it is more desirable that it is the benzene ring.

[0018] n1 and n2 express the integer from which n1+n2 turn into 0-2. As for n1 and n2, it is desirable that either is 0. when n1 or n2 is 2, even if two or more L1, L2, Cy1, and Cy2 are the same,

they may differ.

[0019] the polymerization nature liquid crystal compound of this invention -- following general formula (II): -- [Formula 9]

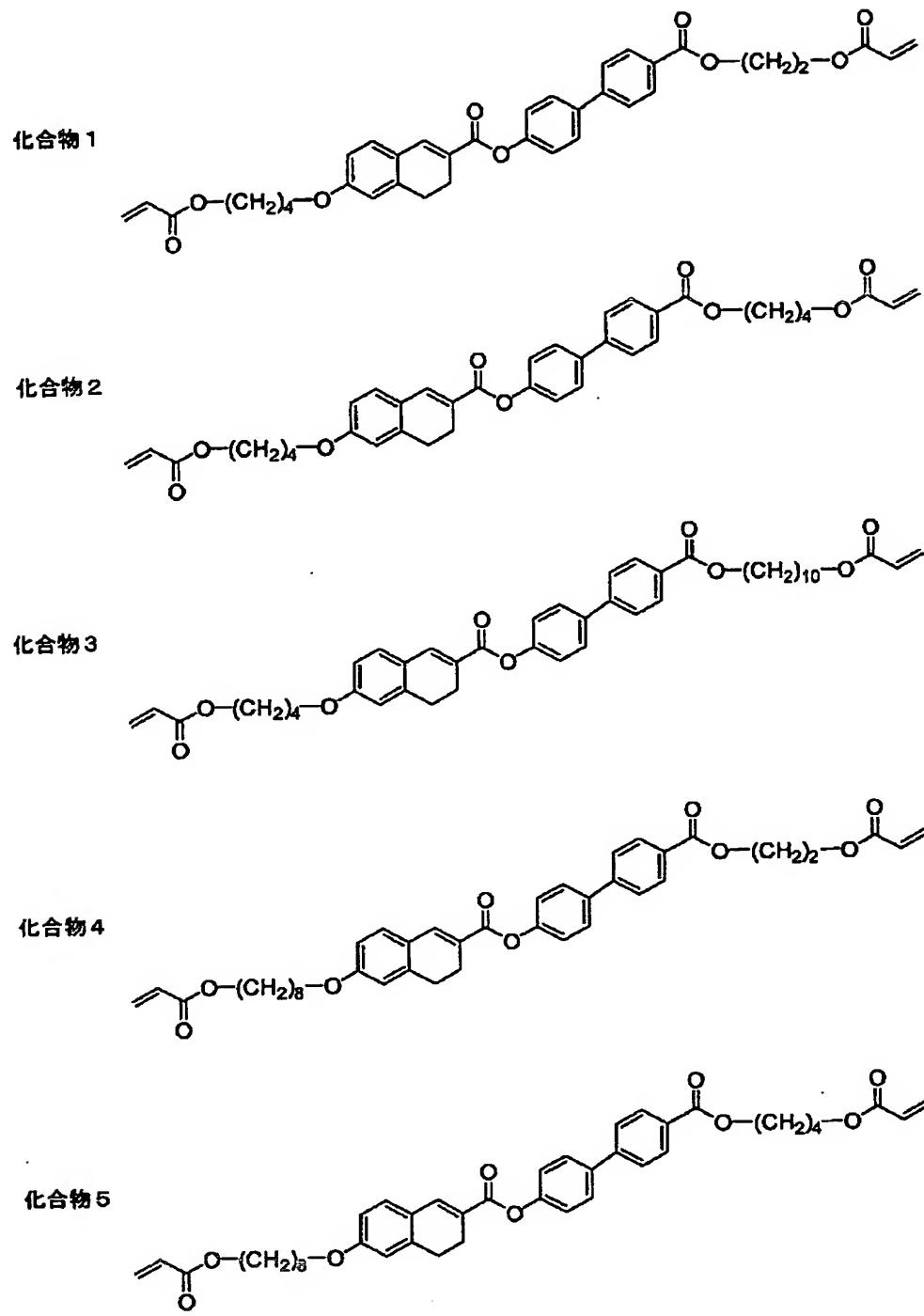


It is desirable for it to be alike and to be expressed more. P1, P2, A1, A2, S1, and S2 in a general formula (II) are synonymous with them in the above-mentioned general formula (I). X expresses the imino group which is not permuted [ an oxygen atom, a sulfur atom, a permutation, or ] among a general formula (II). As for X, it is desirable that it is an oxygen atom.

[0020] Although the example of the polymerization nature liquid crystal compound of this invention is shown below, this invention is not limited to them.

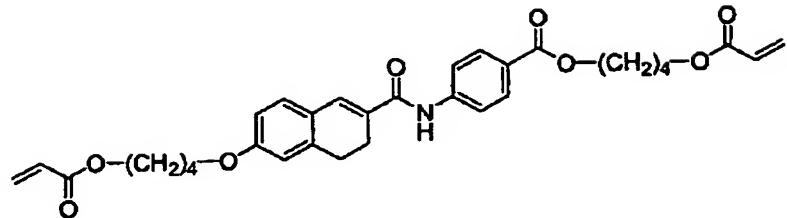
[0021]

[Formula 10]

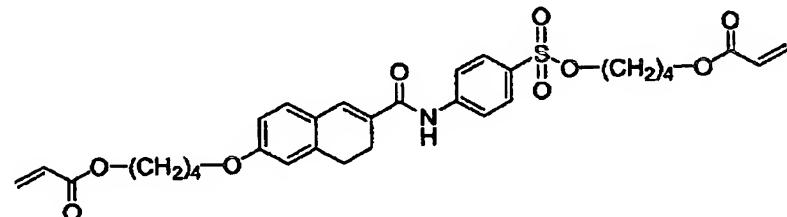


[0022]  
[Formula 11]

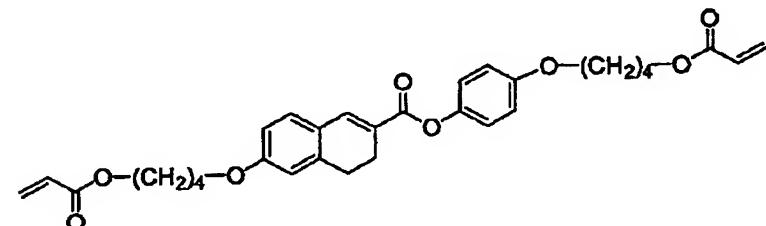
化合物 6



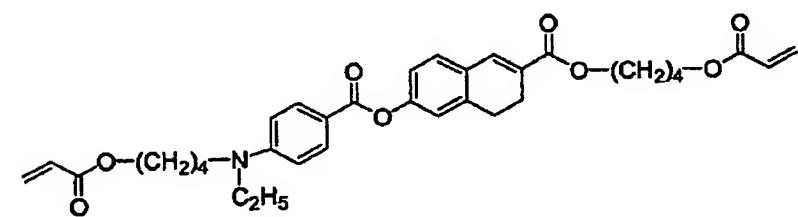
化合物 7



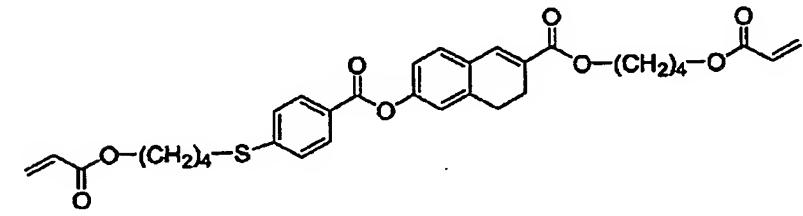
化合物 8



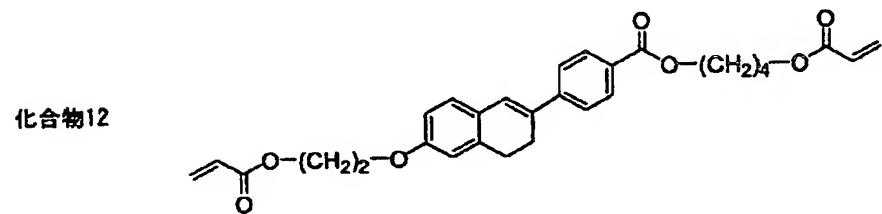
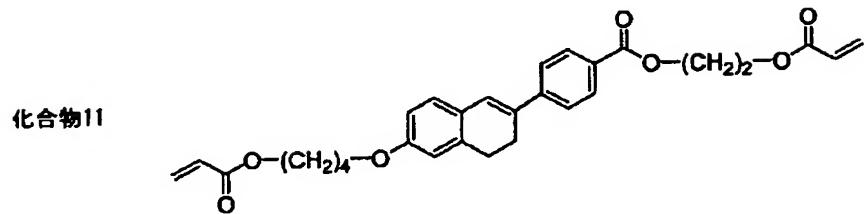
化合物 9



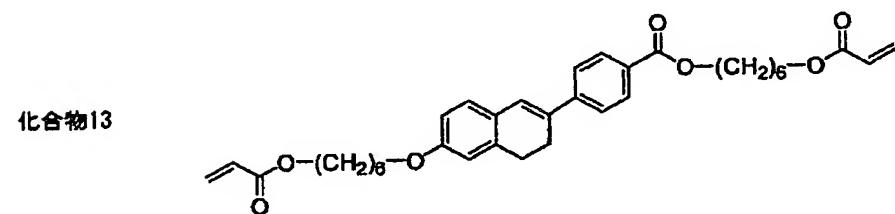
化合物10



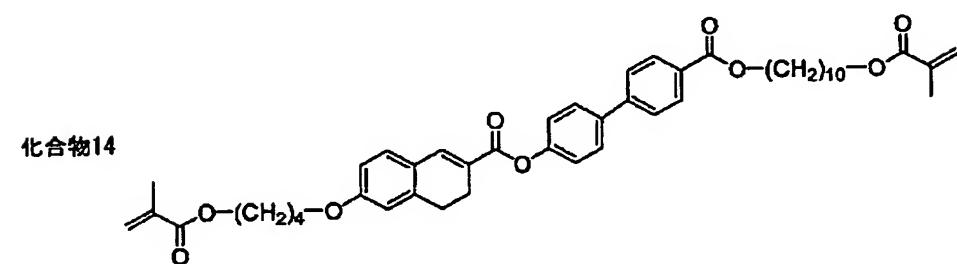
[0023]  
[Formula 12]



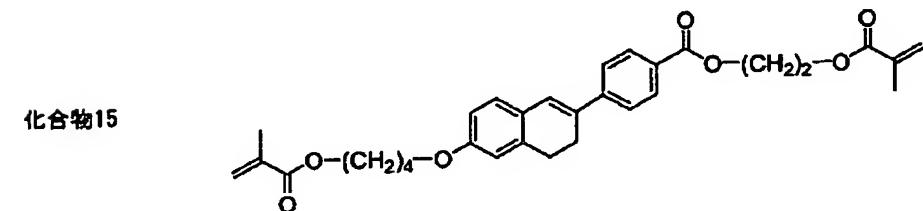
### 化合物12



### 化合物13



化合物14

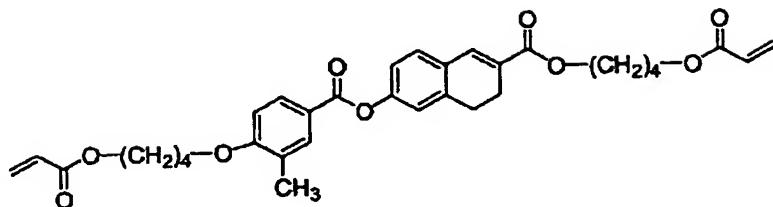


化合物15

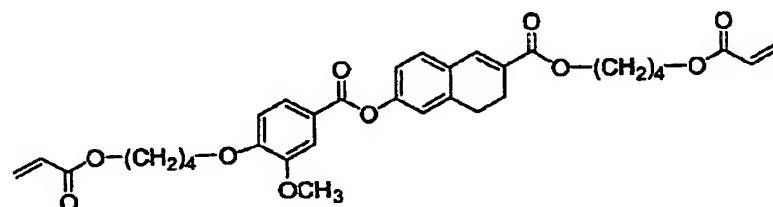
[0024]

[Formula 13]

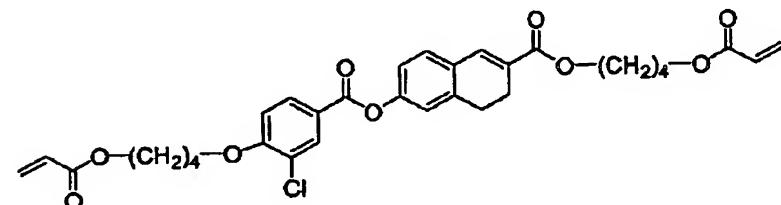
化合物16



化合物17

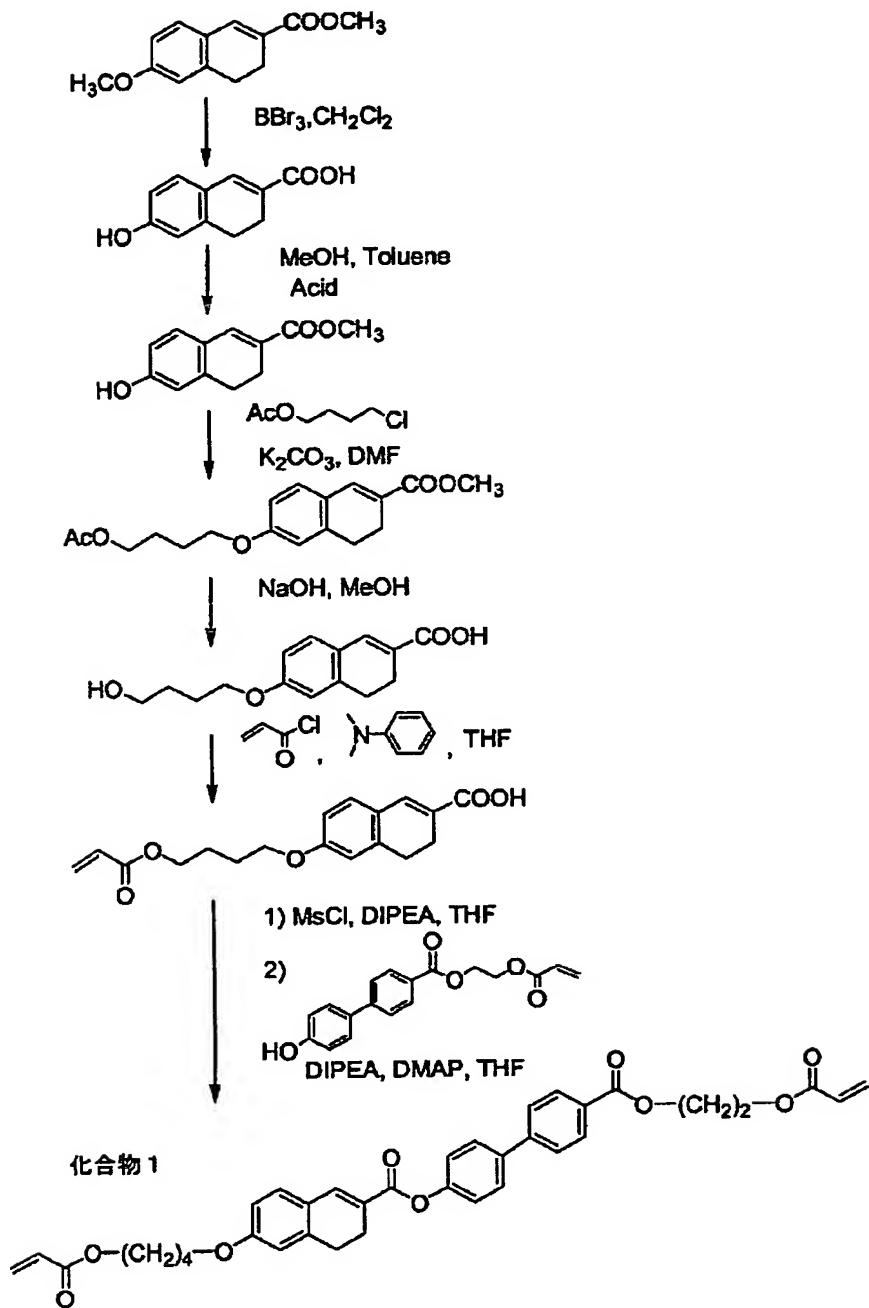


化合物18

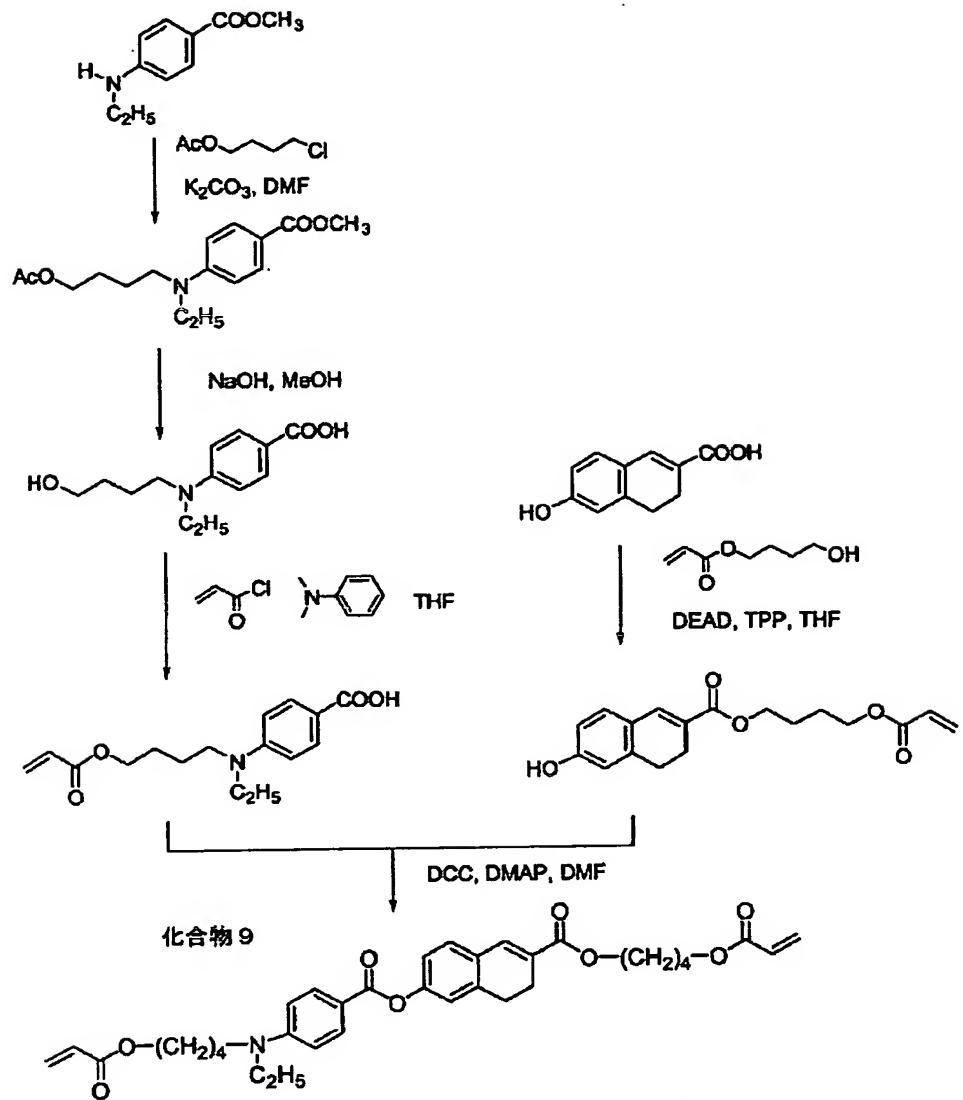


[0025] For example, the synthesis method of compounds 1, 9, and 11 is shown below. The polymerization nature liquid crystal compound of this invention is compoundable according to these synthesis methods. However, this invention is not limited to these.

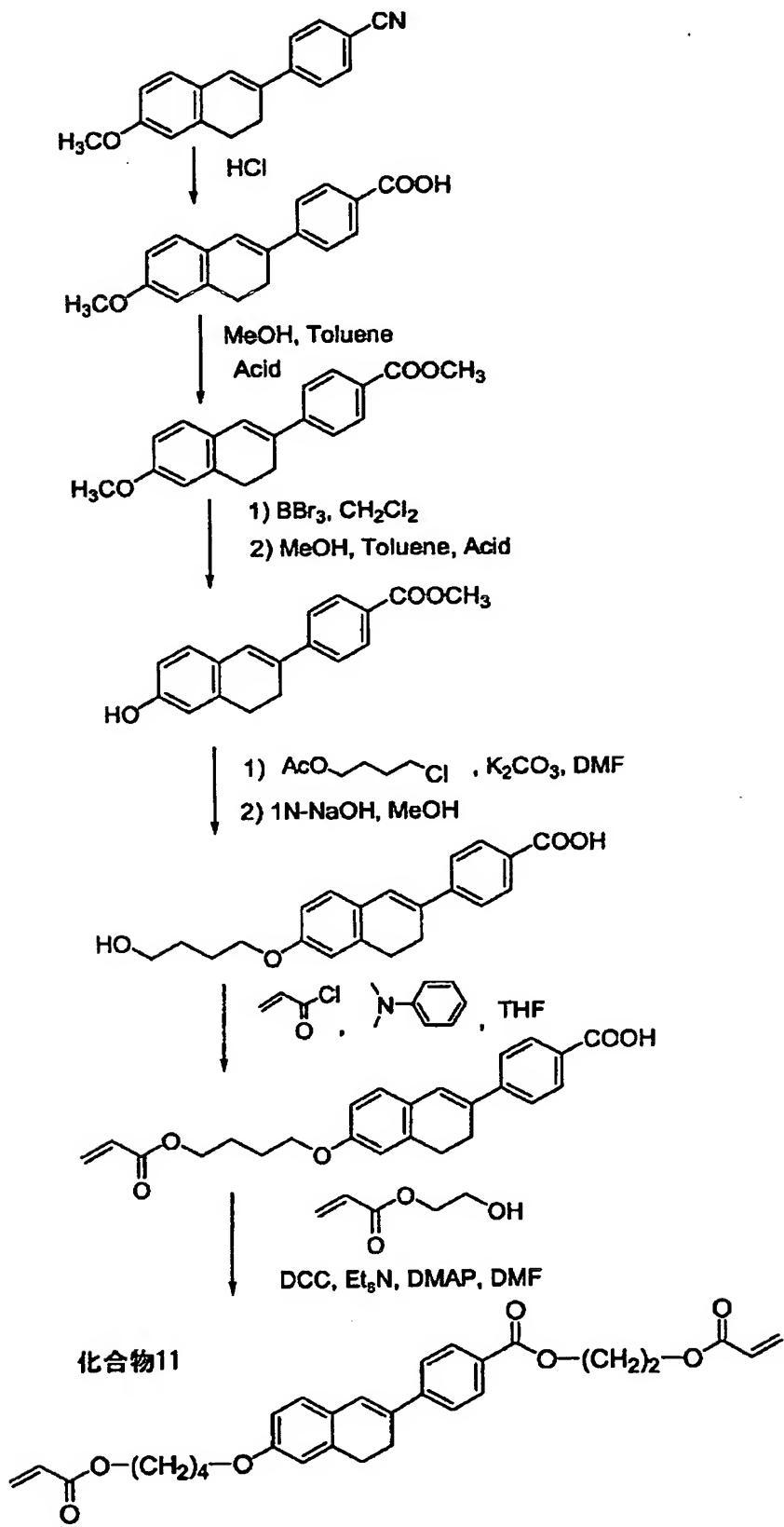
[0026] The synthetic example of a compound 1 [\*\* 14]



[0027] The synthetic example of a compound 9 [\*\* 15]



[0028] The synthetic example of a compound 11 [\*\* 16]



[0029] [2] It is characterized by the polymerization nature liquid crystal compound of above-mentioned this invention coming to carry out the polymerization of the liquid crystal polymer of liquid crystal polymer this invention. It can manufacture using general technique, for example, the liquid crystal polymer of this invention is (a). The liquid crystal constituent which contains the polymerization nature liquid crystal compound of this invention in base materials, such as a glass

plate, is applied, and it is (b). It can manufacture by carrying out the polymerization of the polymerization nature liquid crystal compound, where orientation is carried out.

[0030] (a) Although especially the base material used for manufacture of the spreading polymer of a liquid crystal constituent is not limited, as a desirable example, a glass plate, a high polymer film, a reflecting plate, etc. are mentioned. A liquid crystal constituent makes the polymerization nature liquid crystal compound of this invention contain additives, such as a suitable polymerization initiator, polymerization inhibitor, a photosensitizer, a cross linking agent, and a liquid crystal orientation assistant, if needed with a solvent. It is easy to be well-known [ an additive ]. Although especially the amount of the additive added to a liquid crystal constituent is not limited, the total quantity of an additive makes the whole liquid crystal constituent 100 % of the weight, it is desirable that it is 30 or less % of the weight, and it is more desirable that it is 15 or less % of the weight. A solvent is not restrictive, for example, a tetrahydrofuran (THF) etc. is mentioned. A well-known approach can be used as an approach of applying a liquid crystal constituent to a base material, for example, the curtain coating method, an extrusion coating method, the roll coating method, a spin coating method, a DIP coating method, a bar coating method, a spray coating method, a slide coating method, a printing coating method, etc. can be used.

[0031] (b) As the approach of carrying out orientation of the orientation polymerization nature liquid crystal compound, the method of performing orientation processing in advance is mentioned, for example to an above-mentioned base material. The liquid crystal orientation layer which becomes a base material from various polyimide system orientation film, the polyvinyl alcohol system orientation film, etc. as a desirable method of performing orientation processing is prepared on a base material, and the method of processing rubbing etc. is mentioned. Moreover, as the approach of carrying out orientation of the polymerization nature liquid crystal in a liquid crystal constituent, the method of impressing a magnetic field, electric field, etc. to the liquid crystal constituent on a base material etc. is mentioned. When using a liquid crystal polymer for a nonlinear optical element or an electro-optics component, it is desirable by impressing electric field to carry out orientation of the polymerization nature liquid crystal compound. The method of the approach of impressing direct-current electric field, for example, the method of using corona discharge, etc. being mentioned as an approach of impressing electric field, and using corona discharge is desirable.

[0032] (c) The polymerization of the polymerization liquid crystal constituent can be carried out by the well-known method of using heat or an electromagnetic wave. The radical polymerization which irradiates ultraviolet radiation, using a photopolymerization initiator as a polymerization reaction by the electromagnetic wave is desirable. Moreover, it is also desirable to construct a bridge, impressing a magnetic field and electric field. Although the liquid crystal polymer formed on the base material may be used for the optical phase contrast film, an optically anisotropic body, a nonlinear optical element, an electro-optics component, etc. as it is, if needed, it may exfoliate from a base material or you may imprint to other base materials.

[0033] [3] The liquid crystal polymer of application this invention can be used suitable for the optical phase contrast film, an optically anisotropic body, a nonlinear optical element, an electro-optics component, etc. Since these application itself is well-known, it is as follows when it explains briefly. The optical phase contrast film and an optically anisotropic body can be used as the phase contrast film of a liquid crystal display, the optical compensating plate (phase contrast plate) of a liquid crystal display, a polarization beam splitter, etc. A nonlinear optical element and an electro-optics component can be used for for example, a waveguide mold light modulation element, an optical switch, etc.

[0034]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these.

[0035] example 1 Bull.Chem.Soc.Fr. magazine 1 of 21.8 g compounded by the approach indicated by 512 pages (1950), and 2-dihydro-7-methoxy naphthalene-3-carboxylic-acid methyl -- the dichloromethane of 218 mL -- dissolving -- Tori -- bromination -- dichloromethane solution 218 mL (1.68 M) of boron was added. After stirring the obtained solution at a room temperature for 2 hours, it flowed into iced water, and 1 of 19 g which precipitated, and 2-dihydro-7-hydroxy naphthalene-3-carboxylic acids were collected by suction filtration.

[0036] The toluene of 500 mL was made to distribute the obtained 1 and 2-dihydro-7-hydroxy naphthalene-3-carboxylic acid, and the methanol of 30 mL and 2g Para toluenesulfonic acid were added and heated, and it stirred under reflux for 8 hours, removing the water produced at the reaction by Dean Stark. Reaction mixture was washed with water after that, and it condensed under reduced pressure. The obtained residue was made to recrystallize in an acetonitrile and 1 of 17.2 g and 2-dihydro-7-hydroxy naphthalene-3-carboxylic-acid methyl were obtained.

[0037] 3.0 g was dissolved in DMF among 1 obtained and 2-dihydro-7-hydroxy naphthalene-3-carboxylic-acid methyl, the potassium carbonate of the acetoxy butyl chloride of 2.4 g and 3.5 g and the iodine sodium of 0.15 g were added, and it heated at 100 degrees C, and stirred for 8 hours. Water was added to the reaction mixture after stirring, and ethyl acetate extracted. The extract was dried with the sodium sulfate and it condensed under reduced pressure. The silica gel chromatography (an eluate is ethyl-acetate:hexane =2:8) refined the residue, and 1 of 3.0 g and 2-dihydro-7-(4-acetoxy butyloxy) naphthalene-3-carboxylic-acid methyl was obtained.

[0038] 3.0 g was dissolved in the methanol among 1 obtained and 2-dihydro-7-(4-acetoxy butyloxy) naphthalene-3-carboxylic-acid methyls, 1N-sodium-hydroxide water solution was added, and it stirred at 60 degrees C for 5 hours. The hydrochloric acid was added and the 1 of 2.7 g and 2-dihydro-7-(4-hydroxy butyloxy) naphthalene-3-carboxylic acid was obtained after it added water to the reaction mixture after stirring and ethyl acetate washed until it became acidity.

[0039] 2.7 g was dissolved in THF of 50 mL among 1 obtained and 2-dihydro-7-(4-hydroxy butyloxy) naphthalene-3-carboxylic acids, the N,N-dimethylaniline of 1.6 g and the acryloyl chloride of 1.03 mL were added, and it stirred for two days at the room temperature. The obtained reaction mixture was added to water and ethyl acetate extracted. After drying an extract with a sodium sulfate, the 1 of 2.4 g and 2-dihydro-7-(4-acryloyloxy butoxy) naphthalene-3-carboxylic acid was obtained by condensing under reduced pressure and washing the generated solid-state by the hexane.

[0040] Next, the mesyl chloride of 1.0 g was dissolved in THF of 5mL(s), 1 of 2.4 g, a 2-dihydro-7-(4-acryloyloxy butoxy) naphthalene-3-carboxylic acid, the diisopropyl ethylamine of 1.0 g, and the mixed liquor of THF of 5mL(s) were dropped, and it stirred under ice-cooling for 1 hour. Then, to reaction mixture, it is the 4-hydroxy biphenyl-4'-carboxylic acid of 2.36 g. 2-acryloyloxyethyl, the diisopropyl ethylamine of 1.0 g, and the mixed liquor of THF of 5mL(s) were added. The obtained reaction mixture was stirred at the room temperature for 8 hours, water was added, and ethyl acetate extracted. After drying an organic layer with a sodium sulfate, it condensed under reduced pressure. The residue was refined using the silica gel chromatography (an eluate is dichloromethane:ethyl-acetate =95:5), and the compound 1 of 1.2 g was obtained.

[0041] The structure of the compound compound 1 was checked with the NMR spectrum and MS spectrum, and the phase behavior was investigated.

1 H-NMR:(delta, CDCl<sub>3</sub>)1.8-2.0 (4H, m), 2.72 (2H, m), 2.29 (2H, m), 4.04 (2H, t), 4.25 (2H, t), 4.54 (2H, t), and 4.59 (2H, t), 5.8-5.9 (2H, m), 6.1-6.2 (2H, m), 6.5-6.5 (2H, m) and 6.70 (1H, dd), 6.76 (1H, d), 7.22 (1H, d), and 7.29 (2H, d), 7.64 (2H, d), 7.67 (2H, d), and 7.76 (1H, s), 8.12 Fab MASS (2H, d)+(M+H) =611 phase behavior: 66.3 degree-C-Sx-93.1 degree-C-Sa-146 degree-C-N-153 degree-C-I (Sx-Sa: a smectic phase, N:nematic phase, I:isotropy liquid)

[0042] an example 24 -- instead of [ of - hydroxy biphenyl-4'-carboxylic-acid 2-acryloyloxyethyl ] -- 4-hydroxy biphenyl-4' - carboxylic acid The compound 2 was compounded like the example 1 except having used 4-acryloyloxy butyl. The structure of the obtained compound 2 was checked with the NMR spectrum and MS spectrum, and the phase behavior was investigated.

1 H-NMR:(delta, CDCl<sub>3</sub>)1.6-2.0 (8H, m), 2.72 (2H, m), 2.29 (2H, m), 4.04 (2H, t), 4.25 (2H, t), 4.54 (2H, t), and 4.59 (2H, t), 5.8-5.9 (2H, m), 6.1-6.2 (2H, m), 6.5-6.5 (2H, m) and 6.70 (1H, dd), 6.76 (1H, d), 7.22 (1H, d), and 7.29 (2H, d), 7.64 (2H, d), 7.67 (2H, d), 7.76 (1H, s), 8.12 Fab MASS (2H, d)+(M+H) =639 phase-behavior:116 degree-C-Sc-153 degree-C-I (Sc: a smectic phase, I:isotropy liquid)

[0043] an example 34 -- instead of [ of - hydroxy biphenyl-4'-carboxylic-acid 2-acryloyloxyethyl ] -- 4-hydroxy biphenyl-4' - carboxylic acid The compound 3 was compounded like the example 1 except having used 10-acryloyloxy DESHIRU. The structure of the obtained compound 3 was checked with the NMR spectrum and MS spectrum, and the phase behavior was investigated.

1 H-NMR:(delta, CDCl<sub>3</sub>)1.3-1.5 (12H, m), 1.67 (2H, m), 1.76 (2H, m), and 1.8-2.0 (4H, m), 2.73 (2H, m), 2.90 (2H, m), 4.04 (2H, t), 4.15 (2H, t), 4.25 (2H, t), and 4.33 (2H, t), 5.8-5.9 (2H, m) and 6.1-6.2 (2H, m), 6.5-6.5 (2H, m) and 6.70 (1H, dd), 6.76 (1H, d), 7.20 (1H, d), and 7.29 (2H, d), 7.64 (2H, d), 7.67 (2H, d), and 7.76 (1H, s), 8.13 Fab MASS (2H, d)+(M+H) =723 phase behavior: 43.6 degree-C-Sc-75.5 degree-C-Sa-129 degree-C-I (Sc-Sa: a smectic phase, I:isotropy liquid)

[0044] The compound 4 was compounded like the example 1 except having used acetoxy octyl chloride instead of example 4 acetoxy butyl chloride. The structure of the obtained compound 4 was checked with the NMR spectrum and MS spectrum, and the phase behavior was investigated. 1 H-NMR:(delta, CDCl<sub>3</sub>)1.3-1.5 (8H, m), 1.68 (2H, m), 1.80 (2H, m), and 2.73 (2H, m), 2.90 (2H, m), 3.99 (2H, t), and 4.16 (2H, t), 4.53 (2H, t), 4.59 (2H, t), and 5.8-5.9 (2H, m), 6.1-6.2 (2H, m) and 6.5-6.5 (2H, m), 6.70 (1H, dd), 6.76 (1H, d), and 7.20 (1H, d), 7.29 (2H, d), 7.64 (2H, d), and 7.67 (2H, d), 7.76 (1H, s) 8.13 Fab MASS (2H, d)+(M+H) =667 phase-behavior:37.2 degree-C-Sc-65.7 degree-C-Sa-144.1 degree-C-I (Sc-Sa: a smectic phase, I:isotropy liquid)

[0045] instead of [ of example 5 acetoxy butyl chloride ] -- acetoxy octyl chloride -- using -- 4 -- instead of [ of - hydroxy biphenyl-4'-carboxylic-acid 2-acryloyloxyethyl ] -- 4-hydroxy biphenyl-4' - carboxylic acid The compound 5 was compounded like the example 1 except having used 4-acryloyloxy butyl. The structure of the obtained compound 5 was checked with the NMR spectrum and MS spectrum, and the phase behavior was investigated.

1 H-NMR:(delta, CDCl<sub>3</sub>)1.3-1.5 (8H, m), 1.68 (2H, m), 1.80 (2H, m), 1.8-2.0 (4H, m), 2.73 (2H, m), 2.90 (2H, m), and 3.99 (2H, t), 4.16 (2H, t), 4.25 (2H, t), and 4.39 (2H, t), 5.8-5.9 (2H, m) and 6.1-6.2 (2H, m), 6.5-6.5 (2H, m) and 6.70 (1H, dd), 6.76 (1H, d), 7.20 (1H, d), and 7.29 (2H, d), 7.64 (2H, d), 7.67 (2H, d), and 7.76 (1H, s), 8.13 Fab MASS (2H, d)+(M+H) =695 phase behavior: 39.2 degree-C-Sc-67.3 degree-C-Sa-147.6 degree-C-I (Sc-Sa: a smectic phase, I:isotropy liquid)

[0046] Example 64-hydroxy biphenyl-4'-carboxylic acid It is 4-aminobenzoic acid instead of 2-acryloyloxyethyl. The compound 6 was compounded like the example 1 except having used 4-acryloyloxy butyl. MS spectrum of the obtained compound 6 was measured. Fab MASS+(M+H) =562

[0047] Example 74-hydroxy biphenyl-4'-carboxylic acid It is 4-aminobenzene sulfonic acid instead of 2-acryloyloxyethyl. The compound 7 was compounded like the example 1 except having used 4-acryloyloxy butyl. MS spectrum of the obtained compound 7 was measured.

Fab MASS+(M+H) =598[0048] Example 84-hydroxy biphenyl-4'-carboxylic acid The compound 8 was compounded like the example 1 except having used 4-acryloyloxy butyloxy phenol instead of 2-acryloyloxyethyl. MS spectrum of the obtained compound 8 was measured. Fab MASS+(M+H) =535[0049] A 1 of 19 g obtained like example 9 example 1 and 2-dihydro-7-hydroxy naphthalene-3-carboxylic acid is dissolved in THF of 100 mL, and they are triphenyl phosphine of 40% toluene solution 20 g of a diethyl azo dicarboxy rate, and 30 g, and the acrylic acid of 15 g. 4-hydroxy butyl was added. After stirring reaction mixture for 8 hours, it condensed under reduced pressure. The residue is refined using a silica gel chromatography (an eluate is hexane:ethyl-acetate =7:3), and it is 1 of 27 g, and 2-dihydro. - 7-hydroxy naphthalene-3-carboxylic-acid 4-acryloyloxy butyl was obtained.

[0050] Next, 4-ethylamino methyl benzoate of 18 g was dissolved in DMF of 100 mL, and the potassium carbonate of the acetoxy butyl chloride of 15 g and 27 g and 2g iodine sodium were added, and it heated at 100 degrees C, and stirred for 8 hours. The methanol and 1N-sodium-hydroxide water solution were added to the obtained reaction mixture, and it stirred for further 2 hours. After washing the water layer of reaction mixture with ethyl acetate, sediment which added the hydrochloric acid and was produced was collected and the N-ethyl-N-(4-hydroxy butyl) aminobenzoic acid of 11 g was obtained.

[0051] 2.4 g was dissolved in DMF of 20 mL among the obtained N-ethyl-N-(4-hydroxy butyl) aminobenzoic acids, the N,N-dimethylaniline of 1.2 g and the acryloyl chloride of 1.1 mL were added, and it stirred at the room temperature for 8 hours. Then, the precipitate which added reaction mixture to water and was produced was made to recrystallize in an acetonitrile, and the N-ethyl-N-(4-acryloyloxy butyl) aminobenzoic acid of 1.8 g was obtained.

[0052] It is a 0.30 g, compound 1, and 2-dihydro-7-hydroxy naphthalene-3-carboxylic acid among the obtained N-ethyl-N-(4-acryloyloxy butyl) aminobenzoic acids. Among 4-acryloyloxy butyl, it dissolved in DMF of 10 mL and the dicyclohexylcarbodiimide of 0.36 g and 0.21 g and the

diisopropyl ethylamine of 0.13 g were stirred for 8 hours. Water was added to reaction mixture after that, ethyl acetate extracted, the extract was dried with the sodium sulfate, and it condensed under reduced pressure. The silica gel chromatography (an eluate is chloroform:ethyl-acetate =7:3) refined the residue, and the compound 9 of 0.2 g was obtained. MS spectrum of the compound compound 9 was measured.

Fab MASS+(M+H) =590[0053] The compound 10 was compounded like the example 9 except having used 4-mercaptopbenzoic acid methyl instead of example 104-ethylamino methyl benzoate. MS spectrum of the obtained compound 10 was measured.

Fab MASS+(M+H) =579[0054] 1 of 5.2 g compounded according to the approach of a publication to example 11 JP,59-163358,A and 2-dihydro-3-(4-cyanophenyl)-7-methoxy naphthalene were added to the ethylene glycol monomethyl ether of 50 mL, 2N-sodium-hydroxide water solution of 25 mL was added to the pan, and it stirred under reflux for 12 hours. Water was added to reaction mixture after that, and ethyl acetate washed. The precipitate which added the hydrochloric acid to reaction mixture and was produced was collected, and 1 of 2.6 g and 2-dihydro-3-(4-carboxyphenyl)-7-methoxy naphthalene were obtained.

[0055] The toluene of 50 mL was made to distribute 1 of obtained 2.6 g, and 2-dihydro-3-(4-carboxyphenyl)-7-methoxy naphthalene, and the methanol of 3mL and the Para toluenesulfonic acid of 0.2 g were added and heated, and it stirred under reflux for 8 hours, removing the water produced at the reaction by Dean Stark. Reaction mixture was washed with water after that, and it condensed under reduced pressure. The obtained residue was made to recrystallize in an acetonitrile and 1 of 2.1 g and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-methoxy naphthalene were obtained.

[0056] obtained 2.1 g 1 and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-methoxy naphthalene -- the dichloromethane of 30 mL -- adding -- Tori -- bromination -- the dichloromethane solution (1.68 M) of boron was added 30 mL. After stirring reaction mixture at a room temperature for 2 hours, the produced precipitate which filled iced water with was collected by suction filtration, and 1 of 1.5 g and 2-dihydro-3-(4-carboxyphenyl)-7-hydroxy naphthalene were obtained.

[0057] The toluene of 50 mL was made to distribute 1 of obtained 1.5 g, and 2-dihydro-3-(4-carboxyphenyl)-7-hydroxy naphthalene, and the methanol of 3mL and the Para toluenesulfonic acid of 0.2 g were added and heated, and it stirred under reflux for 8 hours, removing the water produced at the reaction by Dean Stark. Reaction mixture was washed with water after that, and it condensed under reduced pressure. The obtained residue was made to recrystallize in an acetonitrile and 1 of 1.2 g and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-hydroxy naphthalene were obtained.

[0058] 0.52 g was dissolved in DMF of 10 mL among 1 obtained and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-hydroxy naphthalene, and the potassium carbonate of the acetyloxy butyl chloride of 0.48 g and 0.7 g and the iodine sodium of 0.04 g were added, and it heated at 100 degrees C, and stirred for 8 hours. Water was added to reaction mixture after that, and ethyl acetate extracted. The extract was dried with the sodium sulfate and it condensed under reduced pressure.

The silica gel chromatography (an eluate is ethyl-acetate:hexane =2:8) refined the residue, and 0.6g 1 and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-(4-acetyloxy butyloxy) naphthalene were obtained.

[0059] 1 of obtained 0.6 g and 2-dihydro-3-(4-methoxycarbonyl phenyl)-7-(4-acetyloxy butyloxy) naphthalene were dissolved in the methanol, 1N-sodium-hydroxide water solution was added, and it stirred at 60 degrees C for 5 hours. The hydrochloric acid was added and 1 of 0.34 g and 2-dihydro-3-(4-carboxyphenyl)-7-(4-hydroxy butyloxy) naphthalene were obtained after it added water to the reaction mixture after stirring and ethyl acetate washed until it became acidity.

[0060] 1 of obtained 0.34 g and 2-dihydro-3-(4-carboxyphenyl)-7-(4-hydroxy butyloxy) naphthalene were dissolved in THF of 20 mL, the N,N-dimethylaniline of 0.16 g and the acryloyl chloride of 0.25 mL were added, and it stirred for two days at the room temperature. The obtained reaction mixture was added to water and ethyl acetate extracted. After drying an extract with a sodium sulfate, 1 of 0.32 g and 2-dihydro-3-(4-carboxyphenyl)-7-(4-acryloyloxy butyloxy) naphthalene were obtained by condensing under reduced pressure and washing the generated solid-state by the hexane.

[0061] It is the acrylic acid of 0.3 g and 0.1 g among 1 obtained and 2-dihydro-3-(4-carboxyphenyl)-7-(4-acryloyloxy butyloxy) naphthalene. 2-hydroxyethyl, the dicyclohexylcarbodiimide of 0.2 g, the triethylamine of 0.1 g, and a 0.05g dimethylamino pyridine were dissolved in DMF of 10 mL, and it stirred at the room temperature for 8 hours. Water was added to reaction mixture after that, and ethyl

acetate extracted. The extract was dried with the sodium sulfate and it condensed under reduced pressure. The silica gel chromatography (an eluate is chloroform:ethyl-acetate =7:3) refined the residue, and the compound 11 of 0.1 g was obtained. MS spectrum of the obtained compound 11 was measured.  $\text{Fab MASS+}(M+H) = 491[0062]$  Acetyloxy ethyl chloride is used instead of example 12 acetyloxy butyl chloride, and it is an acrylic acid. It is an acrylic acid instead of 2-hydroxyethyl. The compound 12 was compounded like the example 11 except having used 4-hydroxy butyl. MS spectrum of the obtained compound 12 was measured.  $\text{Fab MASS+}(M+H) = 491[0063]$  KISHIRU chloride is used to acetyloxy instead of example 13 acetyloxy butyl chloride, and it is an acrylic acid. It is an acrylic acid instead of 2-hydroxyethyl. The compound 13 was compounded like the example 11 to 6-HIDOROKISHI except having used KISHIRU. MS spectrum of the obtained compound 13 was measured.  $\text{Fab MASS+}(M+H) = 575[0064]$  instead of [ of example 14 acryloyl chloride ] -- meta-acryloyl chloride -- using -- 4 -- instead of [ of - hydroxy biphenyl-4'-carboxylic-acid 2-acryloyloxyethyl ] -- 4-hydroxy biphenyl-4' - carboxylic acid The compound 14 was compounded like the example 1 except having used 10-methacryloyloxy DESHIRU. MS spectrum of the obtained compound 14 was measured.

$\text{Fab MASS+}(M+H) = 751[0065]$  Meta-acryloyl chloride is used instead of example 15 acryloyl chloride, and it is an acrylic acid. It is methacrylic acid instead of 2-hydroxyethyl. The compound 15 was compounded like the example 11 except having used 2-hydroxyethyl. MS spectrum of the obtained compound 15 was measured.

$\text{Fab MASS+}(M+H) = 519[0066]$  The mesyl chloride of example 16 1.3 g was dissolved in THF of 5mL(s), the 3-methyl-4-(4-acryloyloxy butyloxy) benzoic acid of 2.8 g, the diisopropyl ethylamine of 1.3 g, and the mixed liquor of THF of 5mL(s) were dropped, and it stirred under ice-cooling for 1 hour. 1 of 3.2 g compounded by the same approach as an example 9 to the reaction mixture after stirring, 2-dihydro-7-hydroxy naphthalene-3-carboxylic acid 4-acryloyloxy butyl, the diisopropyl ethylamine of 1.3 g, and the mixed liquor of THF of 5mL(s) were added. After stirring reaction mixture at a room temperature for 8 hours, water was added, and ethyl acetate extracted. The extract was dried with the sodium sulfate and it condensed under reduced pressure. The silica gel chromatography (an eluate is dichloromethane:ethyl-acetate =90:10) refined the residue, and the compound 16 of 3.4 g was obtained. MS spectrum of the compound compound 16 was measured.  $\text{Fab MASS+}(M+H) = 577[0067]$  The compound 17 was compounded like the example 16 except having used the 3-methoxy-4-(4-acryloyloxy butyloxy) benzoic acid instead of the example 17 3-methyl-4-(4-acryloyloxy butyloxy) benzoic acid. MS spectrum of the obtained compound 17 was measured.

$\text{Fab MASS+}(M+H) = 593[0068]$  The compound 18 was compounded like the example 16 except having used the 3-chloro-4-(4-acryloyloxy butyloxy) benzoic acid instead of the example 18 3-methyl-4-(4-acryloyloxy butyloxy) benzoic acid. MS spectrum of the obtained compound 18 was measured.

$\text{Fab MASS+}(M+H) = 597[0069]$  After performing rubbing processing to the glass substrate which applied the polyimide system orientation film (SE-150) by example 19 Nissan Chemical Industries, Ltd., the liquid crystal constituent which has the presentation shown in the following table 1 was applied with the spin coating method (1000 rpm, 20 s). The liquid crystal constituent on a substrate was dried and heated continuously (orientation aging), ultraviolet rays were irradiated further and the optical phase contrast film whose thickness is 1.2 micrometers was produced. The refractive-index anisotropy of the bridge formation film measured by ellipsometry was  $\Delta n = 0.29$  (633 nm). Moreover, as conventional optical phase contrast film, it is a Die Angew. Macromol. Chem. magazine, When the bridge formation film was produced using 1 of the 183rd volume and a 45 pages (1990) publication, and 4-phenylene screw (4-[6-(acryloyloxy) hexyloxy] benzoate), the refractive-index anisotropy was  $\Delta n = 0.14$ . It turned out that the optical phase contrast film of this example has the high refractive-index anisotropy compared with the conventional optical phase contrast film.

[0070]

表1 液晶組成物の組成

成分	添加量
化合物1	20.0重量%
セルロースアセテートブチレート	0.02重量%
光重合開始剤 (日本チバガイギー(株)製、イルガキュア651)	0.2重量%
増感剤	0.06重量%
THF	79.72重量%

[0071] The liquid crystal constituent which has the presentation shown in the example 20 following table 2 was applied to the glass substrate with the spin coating method (1000 rpm, 20 s). The liquid crystal constituent on a substrate was set under the corona polling condition (a tungsten needle electrode, 5kV direct-current-voltage impression), and it dried and heated continuously (orientation aging), and ultraviolet rays were irradiated further and the bridge formation film (nonlinear optical element) whose thickness is 0.5 micrometers was produced. To the acquired nonlinear optical element, the infrared light (wavelength: 1.06 micrometers) of YHG laser was irradiated, and generating of a second harmonic was checked. As for the reinforcement of the second harmonic from the produced nonlinear optical element, six months after was held.

[0072]

表2 液晶組成物の組成

成分	添加量
化合物4	10.0重量%
光重合開始剤 (日本チバガイギー(株)製、イルガキュア651)	0.2重量%
増感剤	0.06重量%
THF	89.74重量%

[0073] The liquid crystal constituent which has the presentation shown in example 21 table 2 was applied to the ITO glass substrate with the spin coating method (1000 rpm, 20 s). The liquid crystal constituent on a substrate was set under the corona polling condition (a tungsten needle electrode, 5kV direct-current-voltage impression), and it dried and heated continuously (orientation aging), and ultraviolet rays were irradiated further and the bridge formation film whose thickness is 0.5 micrometers was produced. Next, aluminum was vapor-deposited on the bridge formation film top face, and the electro-optics component was obtained. It is an Appl.Phys.Lett. magazine about the electro-optical effect of the produced electro-optics component, It checked by the approach of the 56th volume and a 1734 pages (1990) publication.

[0074]

[Effect of the Invention] As explained in full detail above, the polymerization nature liquid crystal compound of this invention is excellent as photoelectron high-performance material, and the liquid crystal polymer which consists of this polymerization nature liquid crystal compound is suitable for the optical phase contrast film, an optically anisotropic body, a nonlinear optical element, and an electro-optics component.

[Translation done.]